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THE PHYSICAL CHEMISTRY OF DEFERRIZATION[1]

By Robert Spurr Weston[2]

In the course of human progress, it becomes necessary from time to time to re-state ideas in terms of the day. This necessity is not confined to science and technology, but is the rule where mankind progresses. Even so universal a human element as religion requires for its expression frequent "new bottles" for its "old wine." So, today, we are forced to use new terms to explain the deferrization process and are hopeful that the physical chemist and his colloidal brother will throw new light upon some of the reactions and interferences, now in obscurity. In what follows, the writer will try to restate his own conceptions of the deferrization process in physicochemical language.

While deferrization (and demanganization) is as old as the spring-fed bogs from which organisms and oxygen caused the deposition of iron and the ultimate formation of iron ore, the deferrization process for water is barely a half-century old. Even in such a comprehensive book as William Ripley Nichols' "Water Supply," published in 1883, there is practically no recognition of it and until within a few years the process was applied only to waters from which the iron was removed with great ease, i.e., waters of high pH value, high in bicarbonates and low in "potent" carbon dioxide. Most of these cases were in Europe. In the United States, the process was first applied along the New Jersey shore where conditions were favorable.

In the eighteen-nineties, there occurred cases like Superior, Wisconsin, and Reading, Mass., where the explanation of the results obtained is not found in the reaction formulae, viz.,

A. *Iron as carbonate*

$$2\ FeCO_3 + 2\ CO_2 + 2\ H_2O + 2\ O = 2\ Fe(OH)_2 + O\ (+CO_2)$$

$$2\ Fe(OH)_2 + O + H_2O = Fe_2(OH)_6$$

B. *Iron as sulfate*

$$FeSO_4 + CaCO_3 = FeCO_3 + CaSO_4$$

$FeCO_3$ as in A.

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[1] Read before the Chemical and Bacteriological Section, at the Cleveland Convention, June 9, 1921.

[2] Of Weston & Sampson, Consulting Engineers, 14 Beacon St., Boston.

In one case, good results could be obtained only by limiting the degree of aeration, and in the other by vigorous treatment with lime and sulfate of alumina.

The writer's first conceptions of the process were that iron exists in water as carbonate or sulfate with carbon dioxide or hydrogen sulfide as a solvent. Aeration was necessary to drive off the solvent gases and oxidize the soluble iron to insoluble hydrated oxide, setting free acid in the process. There was little thought of disturbed equilibrium, speed of reaction, electric charges of particles, interfering gels and emulsoids, or the bearing of the hydrogen ion concentration. Even at this writing, our thoughts are fluent. We can neither let the old idols fall, nor place our entire faith in the new and untried.

We now believe that iron in the waters of springs or wells is partly in the form of a salt, partly in the form of a sol of ferrous hydrate, or again in the form of a suspension of compounds of iron with organic matter. When the proportion of solvent—carbonic and other acids—is high and oxygen is absent, the percentage of hydrate sol is negligible or absent.

The steps in the deferrization process are: (1) Aeration and removal of acid; (2) hydrolysis; (3) coagulation.

AERATION AND REMOVAL OF ACID

The absorption of enough oxygen to oxidize the ferrous iron to ferric iron is a simple matter—1 part of oxygen will oxidize 8 parts of iron—but aeration also serves to reduce the carbonic acid to a point where rapid hydrolysis takes place and in the majority of cases should proceed until an equilibrium can be established between ferric hydrate, later removed by coagulation and filtration, and the oxygen on the one hand, and the solvent carbonic and other acids, on the other.

In certain cases, aeration may be carried so far as to upset the relations between part of the iron and the organic matter wherein the presence of a certain amount of carbonic acid seems necessary to prevent the effect of iron upon organic matter. The iron is perhaps in the form of a hydrate sol, protected by a very stable organic sol which latter is neutralized in effect by the presence of carbonic acid.

Much less acid is required to prevent precipitation of manganese than of iron, and in one case it was possible to completely remove the iron and leave the manganese in practically permanent solution simply by stopping the aeration at the proper point.

HYDROLYSIS

Ferrous hydrate is converted to ferric hydrate by hydrolysis, i.e., by the action of water and oxygen; $2Fe(OH)_2 + 2H_2O + O = 2Fe(OH)_3 + H_2O$, the OH of the water combining with the hydrate and the hydrogen combining with the O to form water.

Goodwin states that this is a time reaction, and as it is one of adding OH, the presence of hydrates increases its speed. This is why lime and caustic soda are efficient accelerating agents in deferrization, and why more than enough oxygen is of so little importance. Contrarily, the presence of acids retards hydrolysis.

Hydrolysis is promoted by contact with ferric hydrate already formed and precipitated. Dunbar and Kryck proved that the absorption of oxygen during hydrolysis was much more rapid in a coke filter which had accumulated a considerable bulk of hydrate. The use in our own practice of coke towers of various heights is for this purpose as well as for coagulation. It must be remembered that ferric hydrate is a very weak base, but insoluble, consequently the equilibrium point is very far toward the hydrate side of the equation.

A difficult problem is the hydrolysis of ferrous sulfate, the product being sulfuric acid which, when carbonates are present, reacts to set free carbon dioxide which may reverse the reaction and throw the equilibrium point towards the sulfate side. The obvious remedy is the presence of a hydrate, or aeration prolonged until complete hydrolysis is secured. Sulfates, however, tend to precipitate the ferric hydrate from its sol.

COAGULATION

When hydrolysis is complete, the ferric hydrate exists as a ferric hydrate sol, or colloidal suspension from which the fine particles must be precipitated by gathering them into aggregates large enough to be precipitated by gravity or be caught in the sand layer of a filter.

In pure water, this hydrate would be instantly precipitated from its sol by electrolytes. But natural water contains electrolytes, yet the precipitation of iron is often very difficult. The valency of the electrolyte is an important factor, the sulfates and other bivalent anions being much more potent than chlorine and other univalent anions. For this reason, hard waters usually part with their iron with ease.

Important in this connection are the effects of agitation, friction and contact, and in these respects the phenomena are so similar to those incident to the coagulation of waters with aluminum hydrate that it is hardly worth while to discuss them in detail. Suffice it to say that with some waters, prolonged contact will often allow one to avoid the addition of chemicals.

The effect of temperature is to increase the speed of all the reactions. On the other hand, the rate of absorption of oxygen and gas exchange is decreased.

A type of water hard to purify is the one containing a small amount of iron, say less than 1 p.p.m., and a relatively large amount of peaty organic matter. Here the organic matter seems to act as a protecting colloid and prevents coagulation just as if gelatine, albumen or another emulsoid were present.

Clark showed that such waters could be purified by overloading the positive side of the system, i.e., the iron hydrate, by introducing metallic iron. Obviously aluminum hydrate would have the same effect, although sulfate of alumina, because of its reaction products, which are acid, is not always a successful accelerant.

It is now generally believed that colloidal ferric hydrate, in its dispersed phase, is so maintained by the electric charges of the particles which are positive. If so, the most favorable condition for precipitation is the neutralization of the positive charge due to the absorption of kations by the absorption of anions having negative charges. Thus we find that the precipitating power of an electrolyte depends upon the valency of the ion whose electric charge is negative. Thus, sulfates are more effective than chlorides. Similarly soft ferruginous waters are more difficult to treat than hard.

The natural precipitation of colloids is an interesting phenomenon of deferrization. In 1907, it was found at Posen (Poland) that the colloidal iron in the water from deep wells could be precipitated if mixed in proper proportions with the colored shallow well water containing a colloidal suspension of iron combined with organic matter having negatively charged particles. In this case, precipitation took place when the charges of the particles were neutralized. An excess of either water prevented precipitation, but there existed a zone of precipitation in a series of mixtures of the two waters in ascending and descending amounts respectively. After seeing this interesting experiment, the writer was able to reproduce it using a dark-brown, deep well water from New Orleans, and a clear shallow well water from Massachusetts.

While the presence, side by side, of two waters containing mutually precipitating colloids is not to be met in our practice, it suggests the use of other negative colloids, silica, for example, as reagents for the precipitation of iron. It is only by studies along physico-chemical lines that the deferrization of difficult waters by means other than by vigorous treatment with chemicals may be effected and it is believed that the determination of the hydrogen ion concentration of waters at different stages in the deferrization process will enable us to control it more effectively than at present.